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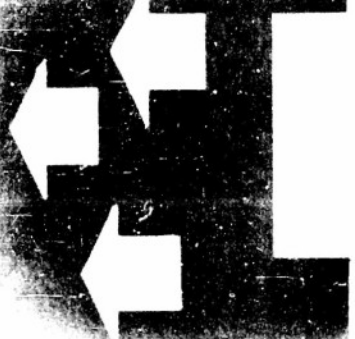
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Report No. 831

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EXPLOSIVES RESEARCH

★
Contract N7onr-46208

Aerojet-General CORPORATION

A SUBSIDIARY OF THE GENERAL TIRE & RUBBER COMPANY
AZUSA, CALIFORNIA



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3 June 1954

Report No. 831

EXPLOSIVES RESEARCH

Contract N7onr-46208

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CONTRACT FULFILLMENT STATEMENT

This quarterly report is submitted in partial fulfillment of
Contract N7onr-46208.

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I. SUMMARY

A. This quarterly report is submitted under Contract N7onr-46208 and covers the period 1 February through 30 April 1954.* The objectives of the contract are to develop new synthetic methods for the preparation of explosives and to prepare new types of explosive compounds.

B. The more important results and conclusions are presented below:

1. New methods for the introduction of nitro groups into aliphatic compounds have been investigated.

a. The nitration of alkyl-substituted malondiamides and cyanoacetamides did not give any nitro compounds.

b. The nitration of diethyl *n*-butylmalonate gave an 83% yield of diethyl *n*-butylnitromalonate. This yield is superior to that reported by Steinkopf (43-48%), who used diethyl methylmalonate.[†] An unstable solid tentatively identified as ammonium ethyl α -nitrocaproate has been obtained in 42% yield from the reaction of diethyl *n*-butylnitromalonate with alcoholic ammonia.

c. Two attempts to nitrate α -acetylbutyrolactone with a mixture of acetic anhydride and nitric acid gave mostly resinous material.

d. An attempt to nitrate acetamidine nitrate with a mixture of nitric acid and fuming sulfuric acid gave a very small yield of acetamide as the only isolable product.

e. The direct nitration of the potassium salt of 2,2,4,6,6-pentanitroheptane with 70% nitric acid or nitrogen tetroxide gave 2,2,4,4,6,6-hexanitroheptane in yields of 39.1 and 43.3%, respectively.

2. In the interest of synthesizing new types of explosive compounds, N-(2,2-dinitropropyl)-trimethylsilylmethylamine and N-(siliconopentyl)-3,3,5,5-tetranitropiperidine have been made. These constitute the first nitro aliphatic and nitro alicyclic silicon compounds that have been prepared.

II. NEW METHODS FOR THE INTRODUCTION OF NITRO GROUPS

A. NITRATION OF SUBSTITUTED MALONIC ACID DERIVATIVES

1. Introduction

In a search for new methods of introducing nitro groups into organic compounds, the direct nitration of functional aliphatic derivatives

* Previous work on this contract was covered in Aerojet Reports No. 512, 538, 562, 589, 621, 637, 660, 682, 711, 737, 770, and 801.
[†] Steinkopf and Supan, Ber. 43, 3239 (1910).

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II New Methods for the Introduction of Nitro Groups, A (cont.)

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seemed to offer the best approach. The National Fireworks Co. has carried out research along this line, studying the direct nitration of malonic and cyanoacetic acid derivatives and their alkyl-substituted derivatives.* They observed that nitration of such compounds as malondiamide and cyanoacetamide gave polynitro compounds, whereas the corresponding alkylated derivatives gave none of the corresponding nitrated products. On the other hand, Steinkopf and Supan prepared diethyl methylnitromalonate by direct nitration of diethyl methylmalonate.† Inasmuch as Steinkopf has successfully nitrated alkyl malonic esters it was believed that other alkyl malonic acid derivatives, such as the alkyl malondiamides, could be successfully nitrated to polynitroparaffins. This report describes the results of the nitrations of substituted malonic acid derivatives.

2. Nitration of n-Butylmalondiamide

a. Discussion

(1) A previous nitration of n-butylmalondiamide using a trifluoroacetic anhydride-nitric acid mixture gave a small quantity of an unidentified oil which analyzed 11.42% in nitrogen.‡ The nitration was repeated in an effort to identify the nitrogenous product, and 11.0 g of n-butylmalondiamide yielded 0.9 g of valeric acid and two nitrogen-containing fractions. One 0.75-g fraction was obtained from the aqueous extract; the bp was 80 to 100°C (at 4 microns), $n_D^{25.3}$ was 1.4431, and N.E. = 175,180. The infrared spectrogram of this material is best interpreted as that of a nitratoacid, probably a nitratocaproic acid.

(2) The second fraction, 0.6 g, was obtained as an oil from the drowned nitration mixture. The bp was 60 to 80°C (at 5 microns), n_D^{25} was 1.4300, and N.E. = 194. An infrared spectrogram gave the same peaks as the 0.75-g fraction, but of different intensities. Accordingly, the second fraction is assumed to be less pure.

b. Experimental

(1) Eleven grams of n-butylmalondiamide was nitrated in a mixture of 39 g of trifluoroacetic anhydride and 23 g of technical 100% nitric acid for 1 hr at 25°C. After the reaction mixture was drowned on 250 g of ice, about 1 g of insoluble oil separated and was taken up in 20 ml of carbon tetrachloride. The aqueous layer was extracted

* National Fireworks Co., Final Summary Report, 1948-1950.

† Cp. cit.

‡ Aerojet Report No. 801, p. 4.

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Groups, A (cont.)

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with ether, and the combined extracts were washed with water and dried over sodium sulfate. After removal of the ether and trifluoroacetic acid 3.3 g of yellow oil was obtained. Distillation at 0.8 mm yielded 0.1 g of liquid (Fraction I), bp 40°C, and 0.9 g of colorless liquid (Fraction II), bp 40°C, $n_D^{25.3}$ 1.4064, neutral equivalent 105. This material was presumed to be

valeric acid. The pot residue which did not distill at 90°C was placed in a bulb tube and distilled at 3μ, giving about 1 g of slightly yellow liquid, bp 88 to 110°C. This was redistilled into two fractions—Fraction III, 0.15 g of colorless liquid boiling at 60 to 80°C/4μ, and Fraction IV, 0.75 g of colorless liquid boiling at 80 to 100°C/4μ, $n_D^{25.3}$ 1.4431. Fraction IV

had the following absorption peaks on an infrared spectrogram: 3.5μ, C-H stretching; 5.82μ, carbonyl group; 6.13μ, nitrate group; 7.85μ, nitrate group; 11.77μ, nitrate group. Other less-well defined peaks were: 2.97μ, probably OH; 9.57μ, probably OH; and 8.03μ carbonyl group. From these data the product is tentatively identified as nitratocaproic acid.

Anal. Calc'd for $C_6H_{11}NO_5$: %C, 40.65; %H, 6.22; %N, 7.92; N.E. = 177.

Found: %C, 43.14; %H, 6.76; %N, 8.64; N.E. = 175, 180.

(2) The water-insoluble oil was distilled under high vacuum, giving 0.8 g of yellow liquid (bp 55 to 95°C/3μ), and a solid pot residue (mp 193 to 198°C). The solid was assumed to be unreacted diamide (mp 200°C). The liquid was redistilled giving Fraction V, bp 60 to 80°C/5μ, $n_D^{25.3}$ 1.4300, N.E. = 194.

Anal. %C, 48.5; %H, 7.45; %N, 4.35.

An infrared spectrogram of this material was similar to that obtained for Fraction IV and is assumed to be a less pure sample of the same material.

3. Nitration of α-Cyanocaproamide

a. Discussion

Nitration of 5.6 g of α-cyanocaproamide with a mixture of nitric and fuming sulfuric acids gave 0.4 g of colorless liquid, bp 55 to 80°C/5μ, n_D^{25} 1.4413. The closest empirical formula that could be assigned to the product corresponds to $C_{11}H_{18}N_4O_6$.

b. Experimental

A 5.6-g quantity of α-cyanocaproamide was dissolved in 13.3 g of 100% technical nitric acid, and 10 ml of fuming (20 to 30% SO₃) sulfuric acid was added dropwise. The temperature was kept at 15°C during

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II New Methods for the Introduction of Nitro Groups, A (cont.)

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the first third of the addition, then between 15 and 17°C during the second third of the addition, and between 19 and 20°C during the remainder of the addition. The mixture was kept at 25 to 30°C during the next 3 hours, until the reaction was over. Gas was evolved and foaming was extensive. The mixture was then poured over 150 g of ice, and a small amount of an oily layer was obtained. The aqueous mixture was extracted with three 50-ml portions of chloroform. The combined extracts were washed with two 50-ml portions of saturated sodium bicarbonate solution. After being dried over sodium sulfate the chloroform was stripped off, leaving less than 1 g of yellow, mobile liquid. Distillation from a bulb tube gave 0.4 g of colorless liquid, bp 55 to 80°C/5 μ , n_D^{25} 1.4413. The infrared spectra indicated the possible presence of nitro groups.

Anal.: %C, 43.80; %H, 5.88; %N, 18.37.

4. Nitration of Diethyl n-Butylmalonate

a. Discussion

(1) Inasmuch as Steinkopf was able to nitrate diethyl methylmalonate and from it prepare the ammonium salt of ethyl α -nitropropionate, and since the influence of other alkyl substituents was unknown, diethyl n-butylmalonate was chosen as a model for the corresponding nitration and decarboxylation reactions.* It has been found that the nitration of diethyl n-butylmalonate with a mixture of acetic anhydride and nitric acid occurs in 83% yield. This is a better yield than that obtained by Steinkopf on the methylmalonate (43 to 48%). The product is diethyl n-butylnitromalonate, bp 93 to 94°C/0.5 mm, n_D^{25} 1.4340, d_4^{25} 1.089 g/ml.

(2) Because nitration of the alkyl malonates involves the use of an excess of nitric and acetic anhydride mixture at 40°C, it was believed that the use of trifluoroacetic anhydride in place of acetic anhydride would prevent the formation of tetranitromethane and reduce the hazard of nitration. However, under these conditions a liquid was obtained (bp 71 to 72°C/0.3 mm, n_D^{25} 1.4294) which analyzed for only 2.36% nitrogen against a calculated value of 5.36% nitrogen. An infrared spectrogram of the material contained additional absorption peaks in comparison with an authentic sample of diethyl n-butylnitromalonate. Apparently trifluoroacetic anhydride enters into the reaction.

(3) Recently (cf II.D) it has been found that the nitration of salts of certain nitro compounds has given gem dinitro

* Ber. 43, 3239 (1910).

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derivatives in reasonable yield where heretofore these compounds were difficult to prepare. Nitration of the salts of ethyl α -nitrocaproate might possibly give the corresponding gem dinitrocaproate. Consequently, attempts have been made to prepare the ammonium and potassium salts of ethyl α -nitrocaproate. Following Steinkopf's procedure for the preparation of ammonium α -nitropropionate, an unstable white crystalline solid was obtained which was tentatively identified as ammonium α -nitrocaproate. It decomposed rather readily, evolving ammonia and giving a liquid of fruity odor. On the melting-point apparatus sintering occurs at 62°C and the compound decomposes up to 80°C, where complete liquefaction occurs. Upon cooling the liquid does not crystallize.

(4) An attempt to prepare the potassium salt of ethyl α -nitrocaproate using alcoholic potassium hydroxide was unsuccessful.

b. Experimental

(1) Ninety-three grams of diethyl n-butyldimaleonate was added dropwise to a refluxing mixture of 150 g of nitric acid and 250 g of trifluoroacetic anhydride at 37 to 39°C. The addition required about 1-1/2 hr, and the solution was refluxed for an additional 1/2 hr and then poured on 1 kg of ice, yielding an oily layer. The solution was then extracted with ether and dried. Evaporation of the ether gave 120 g of yellow oil. Distillation gave the following fractions:

<u>Fraction</u>	<u>bp, °C</u>	<u>n_D^{25}</u>	<u>wt</u>
I	61-79/0.4 mm	1.4298	7.6 g
II	79-82/0.4 mm	1.4303	74.6 g
III	82-89/0.4 mm	1.4330	3.35 g
IV	89-93/0.4 mm	1.4340	6.55 g
V (pot)	>93/0.4 mm	1.4453	8.15 g

Analysis of Fraction II gave 2.36% N (5.36% N was calculated for $C_{11}H_{19}NO_6$). An attempt to form the ammonium salt of α -nitrocaproic ester by solution of the nitromaleonate in ammoniacal ethanol was unsuccessful.

(2) Sixty-two grams of diethyl n-butyldimaleonate was nitrated according to the procedure of Steinkopf, using 100 g of technical 100% nitric acid and 80 g of acetic anhydride.* After the nitration mixture was drowned, and extracted with ether, 75 g of yellow oil was obtained. Distillation gave 62.1 g (83%) diethyl n-butylnitromaleonate, bp 93 to 94°C (0.5 mm), n_D^{25} 1.4340.

Anal. Calc'd for $C_{11}H_{19}NO_6$: %C, 50.57; %H, 7.28; %N, 5.36
Found: %C, 50.03; %H, 7.48; %N, 5.11

* Ber. 43, 3239 (1910)

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(3) Fifty ml of absolute alcohol was saturated with ammonia at ice bath temperature, and 12 g of diethyl n-butylnitromalonate was added. The solution gradually turned orange, but no salt precipitated. After 2 hr ammonia was again bubbled through the solution, and crystallization soon occurred. After ammonia was passed through the solution for an additional 1/2 hr the mixture was cooled and filtered, and the solid was washed with ether. After drying there was obtained 4.0 g of a white, plate-like, crystalline solid which melted over a 20°C temperature range, beginning at 62°C. Upon melting, ammonia was evolved, and a liquid of fruity odor was obtained which did not solidify on cooling. Even at room temperature ammonia was evolved slowly, giving a semi-solid mass.

B. NITRATION OF α -ACETYL BUTYROLACTONE

1. Discussion

a. Inasmuch as the alkyl malonic esters can be easily nitrated, it was of interest to determine the generality of the nitration of carbon atoms containing active hydrogen atoms. One such compound is α -acetyl butyrolactone, which contains a tertiary hydrogen atom adjacent to two carbonyl groups.

b. Two attempts to nitrate 50 g of α -acetyl butyrolactone using a mixture of nitric acid and acetic anhydride resulted in the isolation of 20 to 30 g of dark-red, resinous material. The product appeared to be polymeric and was not further investigated.

2. Experimental

a. α -Acetyl butyrolactone (51 g, 0.4 mole) was added dropwise to a mixture of 40 g of acetic anhydride and 50 g of technical 100% nitric acid at 35 to 40°C. After the addition was complete the mixture was stirred for an additional 10 min, and then cooled to 0°C and poured into 1-1/2 liters of water at 5°C. The resulting clear solution was allowed to stand at room temperature for 1 hr, and was extracted four times with 250-ml portions of ether. The combined ether extracts were washed four times with 100-ml portions of water, then dried over sodium sulfate. Stripping of the ether left 13 g of an unstable orange oil. The oil evolved nitrogen dioxide continuously. It was mostly soluble in water, giving an acidic solution. The oil was taken up in ether and washed with a saturated sodium bicarbonate solution until neutral. Evaporation of the ether left 1.6 g of viscous orange oil which was not characterized.

b. A second nitration, in which the order of addition was reversed (nitrating mixture added to the lactone), gave as product 24 g of a very dark-red, viscous mass which appeared to be polymeric. This material was not investigated further.

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II New Methods for the Introduction of Nitro Compounds (cont.)

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C. NITRATION OF ACETAMIDINE NITRATE

1. Discussion

It was believed that the reactive amidine structure might give useful products if nitrated. Acetamidine hydrochloride was converted to the nitrate salt and nitrated in a mixture of nitric acid and fuming sulfuric acid. However, from 6.0 g (0.05 mole) of acetamidine nitrate about 20 milligrams of product was obtained as a white solid, mp 75 to 77°C. Because the quantity obtained was small, no derivatives could be obtained and further identification was impossible. (However, the closest two-carbon residue melting at that temperature is acetamide. Because the amidine structure is easily hydrolyzed to an amide, this appears reasonable.)

2. Experimental

To a mixture of 15.0 ml of fuming sulfuric acid and 25.0 g of nitric acid was added, portionwise, 6.0 g (0.05 mole) of acetamidine nitrate, keeping the temperature between 10 to 15°C. No apparent reaction occurred. The temperature was slowly raised to 50°C over a period of 2 hr. After the reaction mixture was drowned on 200 g of ice a clear solution resulted. Ether extraction of the solution yielded about 20 mg of a white solid, mp 75 to 77°C. Because the amount was too small to characterize further it was assumed to be acetamide, mp 81°C.

D. NITRATION OF THE POTASSIUM SALT OF 2,2,4,6,6-PENTANITROHEPTANE

1. Introduction

a. The exploration of polynitroparaffins as ingredients for high explosives is seriously handicapped by the limitations of synthetic methods of preparing them. The Shechter-Kaplan method of oxidative nitration* and the Hoffmann tetranitromethane nitration† made a large number of new compounds available. In addition to the factors of cost and yield, both methods have the limitation that they start with the anion of the nitro compounds, and when this anion lacks the desired stability the chances for a successful nitration are nil. In order to circumvent this difficulty, workers at George Washington University‡ prepared nitro derivatives in which

* Ohio State University Research Foundation Project 327, Report No. 26, Nov. 4, 1949; Project 396, Report No. 1, May 15, 1950.

† University of Maryland Progress Report, September 1950 - January 1951, Par I.

‡ George Washington Report, Contract NOrd-9951, Task 3, No. 14, August 5, 1952.

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the aci-configuration was fixed, thus avoiding the anion. They prepared the methyl ester and the acetyl derivative of 2,2,4,6,6-pentanitroheptane and were successful in nitrating these compounds to 2,2,4,4,6,6-hexanitroheptane. In seeking to evaluate this work further, personnel at Hercules Powder Co. nitrated the enol acetate of 2,2,4,6,6-pentanitroheptane.* Other procedures whereby 2,2,4,6,6-pentanitroheptane was treated with potassium acetate, acetic anhydride, and nitrating acid were tried. The yields in most instances were meager and the product impure. Because of the current interest of the Naval Ordnance Laboratory in 2,2,4,4,6,6-hexanitroheptane as a potential explosive, this work was reinvestigated.

b. The work at George Washington University demonstrated that by fixing a secondary nitro group in the aci-configuration by means of the methyl ester or acetyl derivative, nitration could be effected, at least in the case of 2,2,4,6,6-pentanitroheptane, to the corresponding gem dinitro group. It seemed likely that this procedure could be simplified by using a salt of the nitro compound rather than the methyl or acetyl derivative. In treating the salt with a nitrating agent there are two competing reactions. One is the liberation of the free nitro compound and the other is the nitration reaction, where a second nitro group is introduced. In the regeneration of the original nitro compound the aci-configuration is lost and nitration does not occur. The success of the reaction depends on choosing conditions, such as low temperature, wherein the aci-configuration is retained and the nitration step is favored. Accordingly, a study was initiated on the direct nitration of the potassium salt of 2,2,4,6,6-pentanitroheptane. The potassium salt was chosen because of its ease in preparation and handling.

2. Discussion

Two methods have been found for converting the potassium salt of 2,2,4,6,6-pentanitroheptane directly into 2,2,4,4,6,6-hexanitroheptane without proceeding through the intermediate methyl ester or acetyl derivative. The first method, which involved treatment of the potassium salt of 2,2,4,6,6-pentanitroheptane with 70% nitric acid at 5°C, gave in the larger runs (Table I) 72-78.5% yields of a mixture of 2,2,4,6,6-pentanitroheptane and 2,2,4,4,6,6-hexanitroheptane. Reproducible results were not obtained in the smaller runs. Recrystallization of the mixture from Run No. 12 with 70% nitric acid gave a 39.1% yield of pure 2,2,4,4,6,6-hexanitroheptane. The second method involved treatment of the potassium salt of 2,2,4,6,6-pentanitroheptane with a solution of nitrogen tetroxide in carbon tetrachloride at -20°C. The product from this reaction (Run No. 19) was recrystallized from 70% nitric acid to give a 43.3% yield of pure 2,2,4,4,6,6-hexanitroheptane. The use of aqueous nitrogen tetroxide gave only 2,2,4,6,6-pentanitroheptane.

* Hercules Powder Co., Navy Contract NOrd-11280, Task A, Monthly Progress Report, August 25, 1953.

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II New Methods for the Introduction of Nitro Compounds, D (cont.)

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3. Experimental

a. The potassium salt was prepared by dissolving 2,2,4,6,6-pentanitroheptane in ether, adding an ethanolic solution of potassium hydroxide, and precipitating the salt by the addition of an excess of ether. The results are summarized in Table I. The experimental procedures for Runs 12 and 19 are typical.

b. 2,2,4,4,6,6-Hexanitroheptane Obtained from the Potassium Salt of 2,2,4,6,6-Pentanitroheptane and 70% Nitric Acid

Fifty ml of 70% nitric acid was placed in a 200-ml 3-necked flask, fitted with a mechanical stirrer and thermometer. The acid was cooled to 5°C, and 10.8 g of the potassium salt of 2,2,4,6,6-pentanitroheptane was added. The reaction mixture was allowed to warm slowly to room temperature (1 to 2 hr) and then stirred at room temperature (1 to 2 hr). An additional 25 ml of 70% nitric acid was added, and the mixture was heated to 80°C to give a clear solution. The solution was cooled and poured on ice. The white solid was collected, washed with water, and dried; the yield was 8.0 g (72.7%), mp 88 to 93°C. Two recrystallizations from 70% nitric acid yielded 4.3 g (39.1%), mp 124 to 131°C.* A third recrystallization raised the melting point to 132 to 133°C.

Anal. Calc'd for $C_7H_{10}N_6O_{12}$: %C, 22.71; %H, 2.72; %N, 22.70

Found: %C, 22.53; %H, 2.68; %N, 22.57

c. 2,2,4,4,6,6-Hexanitroheptane Obtained from the Potassium Salt of 2,2,4,6,6-Pentanitroheptane and Nitrogen Tetroxide

A solution of 20 ml of nitrogen tetroxide in 50 ml of dry carbon tetrachloride was placed in a 200-ml 3-necked flask, fitted with a mechanical stirrer and thermometer. The solution was cooled to -20°C, and 10.0 g of the potassium salt of pentanitroheptane was added portionwise. The reaction mixture was stirred at -15 to -25°C for 4 hr. The white solid was collected, washed with water, and dried in vacuo over potassium hydroxide, 5.7 g, mp 103-107°C. A single recrystallization from a minimum amount of 70% nitric acid gave 4.42 g (43.3%), mp 130 to 131°C. A 0.52-g quantity of white solid, mp 87 to 117°C, was isolated from the filtrate.

*A 0.6-g quantity of 2,2,4,6,6-pentanitroheptane was isolated from the filtrate.

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II New Methods for the Introduction of Nitro
Compounds, D (cont.)

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TABLE I

NITRATION OF POTASSIUM SALT OF 2,2,4,6,6-PENTANITROHEPTANE

Run	Grams K salt	Nitrating Agent	Vol (ml)	Reaction Conditions	Product Recryst.			
					Crude Yield	Product mp°C	from 70% HNO ₃ Yield	mp°C
1	2.0	100% HNO ₃	20	5 min at 0-5°C	1.4	82-103	0.60	129-132
2	2.0	100% HNO ₃	10	20 min at 0-5°C	1.4	86-105	0.3	128-132
		Ac ₂ O	10					
3	1.8	90% HNO ₃	20	20 min at 0-5°C	1.2	95-101		
4	2.4	70% HNO ₃	25	15 min at 5-7°C	1.0	yellow oil		
5	1.78		25	18 min at 13-15°C	0.75	97-106		
6	1.3			1 hr at 15°C 1 hr at 25°C 1 hr at 32°C	1.2	95-103		
7	1.23			16 min at 29-31°C	0.72	103-108		
8	3.0			1 hr at 30°C	2.0	94-97		
9	2.6		25	Salt added at 5°C, allowed to warm to 25°C overnight	1.9	90-92		
10	12.4		50	Salt added at 5°C, warmed to 25°C in 1 hr, kept at 25°C for 3 hr	9.9 (78.5%)	90-96	4.7 (37.3%)	124-126
11	10.0		50	30 min at 5°C 60 min at 5-22°C 5 min at 50°C	8.0 (78.5%)	87-92		
12	10.8		50	Salt added at 5°C, allowed to warm to room temp, stirred at 25°C for 2 hr 25 ml conc. HNO ₃ added and mixture warmed to 80°C to effect sol'n, cooled.	8.0 (72.7%)	88-93	4.3 (39.1%)	124-131
13	3.4	70% HNO ₃	30	15 min at 45-50°C	2.3	90-103		

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II New Methods for the Introduction of Nitro
Compounds, D (cont.)

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TABLE I (cont.)

Run	Grams K salt	Nitrating Agent	Vol. (ml)	Reaction Conditions	Crude Yield	Product mp°C	Product Recryst. from 70% HNO ₃	
							Yield	mp°C
14	5.0	70% HNO ₃	50	10 min at 60-65°C	3.4	80-85		
15	2.77	"	25	16 min at 75-80°C	1.8	104-108		
16	5.0	"	40	15 min at 85°C	3.2	75-80		
17	2	N ₂ O ₄	4.5	3 hr at -5°C		97-115	0.6	131-132
18	2	N ₂ O ₄	4.0	2 hr at -20°C		97-115	0.76	131-132
		CCl ₄	10.0					
19	10	N ₂ O ₄	20					
		CCl ₄	50	4 hr at -20°C	5.7	103-107	4.42 (43.3%)	131-132
20	3.8	N ₂ O ₄	2.5	5°C		2,2,4,6,6-Pentanitroheptane separated immediately from the reaction mixture		
		H ₂ O	25					

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III. PREPARATION OF NITRO SILICON COMPOUNDS

A. INTRODUCTION

1. In the interest of synthesizing new types of explosives compounds, the possibilities of preparing nitro-silicon compounds are being investigated. This class of compounds may have some unique properties which are of value in explosives. For example, the molar heat of oxidation of silicon is more than twice that of carbon. Thus, it might be possible to incorporate some of the advantages of a metallized explosive into a single compound.

2. The only nitro-silicon compounds known are those in which a nitro group has been introduced into an aromatic ring. Thus, Kipping* succeeded in nitrating the phenyl group of a number of organo-silicon compounds, and found that in general most of the nitration occurred in the meta position. He reduced these nitro compounds to the corresponding amines and formed derivatives of these with acetic acid and acetone. More recently phenyl-trialkylsilanes† and substituted phenyltrialkylsilanes‡ have been nitrated by the use of copper nitrate.

3. The purpose of the present work was to try to prepare aliphatic and alicyclic nitro-silicon compounds. Aliphatic amines were chosen as the starting materials, since this class of compounds has proven very valuable for the synthesis of high explosives. Compounds containing silicon-nitrogen bonds do not play the important part in organo-silicon chemistry that carbon-nitrogen bonds do in carbon chemistry because of the great ease with which silicon-nitrogen compounds are hydrolyzed to silanols and amines. The first true aliphatic amines, i.e., those in which nitrogen

* F. S. Kipping and J. C. Blackburn, J. Chem. Soc. 1932, 2200;
F. S. Kipping and N. W. Cusa, J. Chem. Soc. 1935, 1088;
F. S. Kipping, and L. L. Loyd, J. Chem. Soc. 79, 449 (1901);
D. Vorlander, Ber. 58, 1900 (1925).

† R. A. Benkeser and P. E. Brumfield, J. Am. Chem. Soc. 73, 4770 (1951).

‡ R. A. Benkeser and H. Landesman, J. Am. Chem. Soc. 76, 904 (1954).

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III Preparation of Nitro Silicon Compounds, A (cont.)

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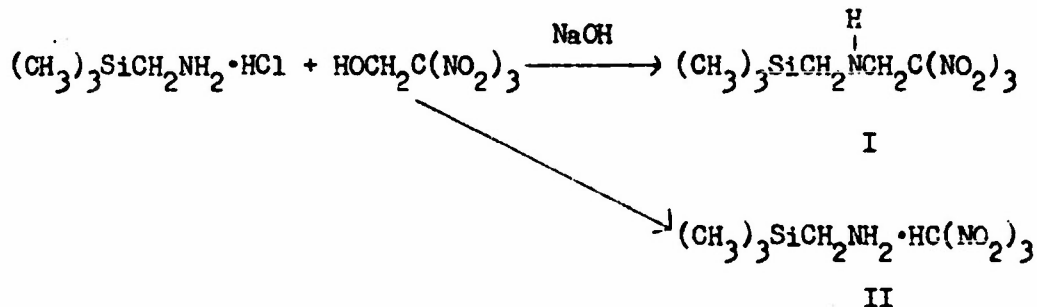
is bound to carbon, in organo-silicon chemistry were synthesized by Sommer and Rockett.* One of these compounds, trimethylsilylmethylamine, was selected as the starting material for the attempted preparation of aliphatic and alicyclic nitro silicon compounds.

4. The preparation of aliphatic secondary polynitroamines by the Mannich condensation of polynitroalcohols and polynitroamines has been previously reported.† Most of the present work is concerned with the condensation of trimethylsilylmethylamine and polynitroalcohols.

B. PREPARATION OF THE NITROFORM SALT OF TRIMETHYLSILYLMETHYLAMINE

1. Discussion

The condensation of trimethylsilylmethylamine hydrochloride and 2,2,2-trinitroethanol in the presence of an equivalent amount of base did not give the desired N-(2,2,2-trinitroethyl)-trimethylsilylmethylamine (I), but rather the nitroform salt of trimethylsilylmethylamine (II).



Similar results were obtained even when the reaction was carried out in a buffered solution.

2. Experimental

In a 100-ml 3-necked flask, fitted with a mechanical stirrer and dropping funnel, was placed 1.4 g (0.01 mole) of trimethylsilylmethylamine hydrochloride, 1.8 g (0.01 mole) of 2,2,2-trinitroethanol, and 20 ml of water. A solution of 0.4 g (0.01 mole) of sodium hydroxide in 10 ml of water was added dropwise at room temperature. A yellow solid immediately precipitated, which was collected, washed with water, and dried. The yield was 1.0 g (39.4%), mp 125 to 130°C dec. Recrystallization from methyl ethyl ketone-ether gave yellow plates melting at 132 to 133°C dec.

* J. Am. Chem. Soc. 73, 5130 (1951).

† Aerojet Reports No. 621, 660, 682, and 770.

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III Preparation of Nitro Silicon Compounds, B (cont.)

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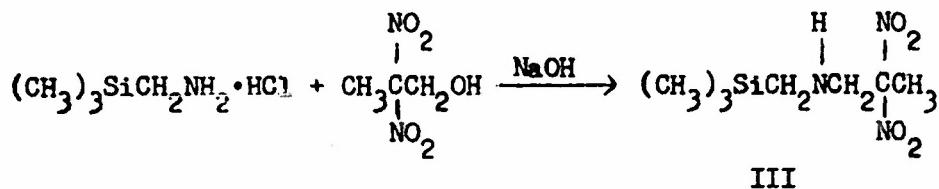
Anal. Calc'd for $C_5H_{14}N_4O_6Si$: %C, 23.62; %H, 5.55; %N, 22.04

Found: %C, 22.95; %H, 5.23; %N, 21.56

C. PREPARATION OF N-(2,2-DINITROPROPYL)-TRIMETHYLSILYLMETHYLAMINE

1. Discussion

The condensation of trimethylsilylmethylamine and 2,2-dinitropropanol gave the desired N-(2,2-dinitropropyl)-trimethylsilylmethylamine (III).



Compound III is the first aliphatic nitro silicon compound to be synthesized. It is a yellow liquid, bp 57 to 64°C (14 microns), n_D^{25} 1.4539.

2. Experimental

In a 200-ml 3-necked flask, fitted with a mechanical stirrer and dropping funnel, was placed 14.0 g (0.10 mole) of trimethylsilylmethylamine hydrochloride, 15.0 g (0.10 mole) of 2,2-dinitropropanol, and 50 ml of water. A solution of 4.0 g (0.10 mole) of sodium hydroxide in 30 ml of water was added dropwise at room temperature. A yellow oil separated and the reaction mixture was extracted with ether. The ether extracts were dried and concentrated to give 18.2 g (77.4%) of yellow oil. The product was distilled from a bulb tube, bp 57 to 64°C (14 micron), n_D^{25} 1.4539. When permitted to stand the yellow liquid partially crystallized.

Anal. Calc'd for $C_7H_{17}N_3O_4Si$: %C, 35.72; %H, 7.29; %N, 17.86; %Si, 11.93

Found: %C, 35.72; %H, 7.28; %N, 17.67; %Si, 11.56

D. PREPARATION OF N-(SILICO-NEOPENTYL)-3,3,5,5-TETRANITROPIPERIDINE

1. Discussion

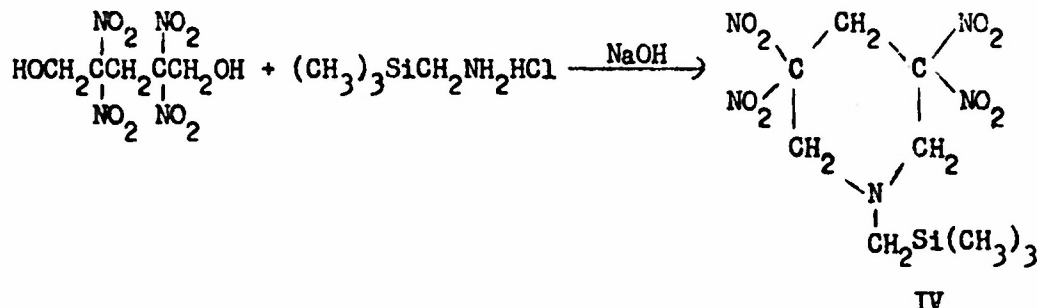
The formation of 3,3,5,5-tetranitropiperidine by the Mannich condensation of 2,2,4,4-tetranitro-1,5-pentanediol and ammonium

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III Preparation of Nitro Silicon Compounds, D (cont.)

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acetate has been previously reported.* In a similar manner N-(silico-neopentyl)3,3,5,5-tetranitropiperidine (IV) has now been prepared by the condensation of 2,2,4,4-tetranitro-1,5-pentanediol and trimethylsilylmethylamine.



Compound IV is the first alicyclic nitro silicon compound to be synthesized. It is a white solid, mp 88 to 90°C dec.

2. Experimental

In a 100 ml 3-necked flask, fitted with a mechanical stirrer and dropping funnel, was placed 3.84 g (0.01 mole) of 2,2,4,4-tetranitro-1,5-pentanediol, 1.4 g (0.01 mole) of trimethylsilylmethylamine hydrochloride, and 50 ml of water. The reaction mixture was warmed to 35°C to effect solution. A solution of 0.4 g (0.01 mole) of sodium hydroxide in 10 ml of water was added dropwise. The cream-colored solid which separated was collected, washed with water, and dried. The yield was 0.6 g (17.1%), mp 80 to 85°C dec. Recrystallization from isopropyl alcohol-water raised the melting point to 88 to 90°C dec.

Anal. Calc'd for $\text{C}_9\text{H}_{17}\text{N}_5\text{O}_8\text{Si}$: %C, 30.77; %H, 4.88; %N, 19.94; %Si, 7.99

Found: %C, 30.84; %H, 4.69; %N, 19.97; %Si, 7.78

E. ATTEMPTED PREPARATION OF 2,2-DIMETHYL-7,7-DINITRO-3,11-DISILA-5,9-DIAZA-TRIDECANE

1. Discussion

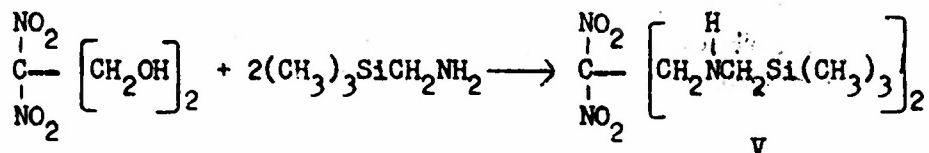
The Mannich condensation of 2,2-dinitro-1,3-propanediol and trimethylsilylmethylamine was expected to yield 2,2-dimethyl-7,7-dinitro-3,11-disila-5,9-diaza-tridecane (V).

* Aerojet Report No. 621

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III Preparation of Nitro Silicon Compounds, E (cont.)

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The product obtained from this reaction was a white solid, mp 128 to 129°C dec, but its analysis did not correspond to that of V, nor could any empirical formula be assigned to it.

2. Experimental

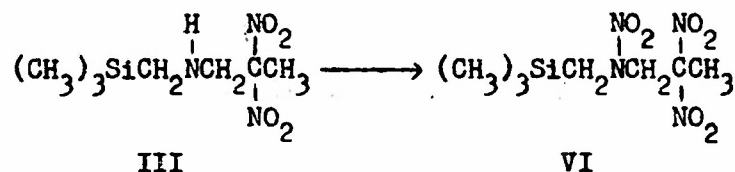
In a 100-ml 3-necked flask, fitted with a mechanical stirrer and dropping funnel, was placed 0.53 g (0.005 mole) of 2,2-dinitro-1,3-propanediol, 1.4 g (0.01 mole) of trimethylsilylmethylamine hydrochloride, and 10 ml of water. A solution of 0.82 g (0.01 mole) of sodium acetate in 5 ml of water was added dropwise. A clear yellow solution was formed which gradually turned cloudy, and after 1 hr a cream-colored solid separated. The yield was 0.7 g, mp 120 to 123°C dec. Recrystallization from dimethylformamide-ether gave a white solid, mp 128 to 129°C dec.

Anal. Calc'd for $\text{C}_{11}\text{H}_{28}\text{N}_4\text{O}_4\text{Si}_2$: %C, 39.26; %H, 8.39; %N, 16.65; %Si, 16.68

Found: %C, 28.91; %H, 6.68; %N, 18.95; %Si, 11.09

F. ATTEMPTED PREPARATION OF N-(2,2-DINITROPROPYL)-TRIMETHYLSILYL-METHYLNITRAMINE

The attempt to convert N-(2,2-dinitropropyl)-trimethylsilylmethylamine (III) to the corresponding nitramine (VI) has thus far been unsuccessful:



The nitrations were carried out with a mixture of 100% nitric acid and acetic anhydride, with copper nitrate, and with nitrogen tetroxide. In each case only small amounts of unstable oils were obtained.

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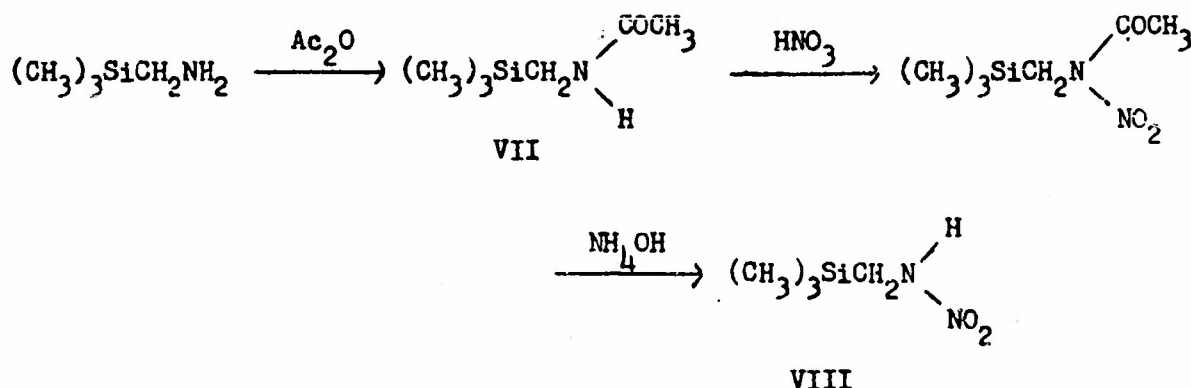
III Preparation of Nitro Silicon Compounds (Cont.)

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G. PREPARATION AND NITRATION OF N-ACETYL TRIMETHYLSILYLMETHYLAMINE

1. Discussion

In the interest of preparing a silicon compound containing a nitramino group, an attempt was made to prepare trimethylsilylmethylnitramine (VIII) by the following series of reactions:



Acetylation of trimethylsilylmethylamine gave N-acetyl trimethylsilylmethylamine (VII), a white crystalline solid, mp 45 to 47°C. Nitration of VII with a mixture of 100% nitric acid and acetic anhydride gave an oil of unknown constitution. Analysis showed that the oil contained both silicon and nitrogen, thus indicating that the silyl amine was not totally cleaved by strong acid.

2. Experimental

In a 100-ml 3 necked flask, fitted with a mechanical stirrer and dropping funnel, was placed 5 g (0.036 mole) of trimethylsilylmethylamine hydrochloride, 25 ml of water, and 25 ml of ether. A solution of 1.4 g (0.036 mole) of sodium hydroxide in 5 ml of water was added dropwise. The ether solution was separated, the aqueous layer was extracted with ether, and the ether extracts were combined and dried. Five ml of acetic anhydride was added to the ether solution, and the reaction mixture was refluxed for 2 hr. The solution was concentrated to give 3.0 g (58%) of oil. A sample (bp 74 to 76°C at 11 microns) was distilled from a bulb tube to give a colorless liquid which solidified in white plates. The melting point was 45 to 47°C.

Anal. Calc'd for $\text{SiC}_6\text{H}_{15}\text{NO}$: %C, 49.61; %H, 10.41; %N, 9.64.

Found: %C, 49.29; %H, 10.04; %N, 9.85.

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III Preparation of Nitro Silicon Compounds, G (cont.)

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A solution of 0.9 g of N-acetyl trimethylsilylmethylamine in 10 ml of acetic anhydride was added to 10 ml of 100% nitric acid at 5°C. The solution was poured on ice and extracted with ether. The ether extracts were dried and concentrated to give 0.25 g of yellow liquid, bp 75 to 78°C (7 microns).

Anal. Calc'd for $\text{SiC}_5\text{H}_{11}\text{N}_2\text{O}_3$: %Si, 14.72; %N, 14.70.

Found: %Si, 18.43; %N, 7.77.

IV. PREPARATION OF SAMPLES FOR EVALUATION BY THE NAVAL ORDNANCE LABORATORY

The following samples were prepared and submitted to the Naval Ordnance Laboratory for evaluation:

A. bis(2,2,2-TRINITROETHYL)-4,7-DINITRAZA DECANEDIOATE

This compound was originally of interest because it had the unusual combination of good crystal density (1.72), insensitivity to impact (227 cm/2.5 kg, 13 shots), and excellent thermal stability at 100°C. A larger sample was submitted for further evaluation. With the larger sample the impact sensitivity was redetermined more accurately in a 50-shot test, and the detonation velocity was measured. The impact sensitivity of this second sample was 126 cm/2.5 kg, a sensitivity between that of TNT and Composition B. The detonation velocity appears to be approximately 350 meters/sec greater than that of TNT at corresponding densities. The combination of less attractive impact sensitivity and only slight superiority over TNT in detonation velocity makes the compound less interesting. However, some work on phase systems with other explosives will be carried out.

B. bis(2,2,2-TRINITROETHYL)-2,4,7-TRINITRAZA OCTANEDIOATE

a. This compound was found to have the following properties:

- (1) Impact sensitivity, 11 cm/2.5 kg, Class 5
- (2) Hot-bar ignition temperature, 178°C
- (3) Vacuum stability, 27.5 ml of gas in 48 hr at 100°C, Class IV
- (4) Crystal density, 1.38

The compound is too sensitive and unstable to be of interest.

C. 2,2,4,4,6,6-HEXANITROHEPTANE

An additional sample of this compound was submitted for further evaluation.

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